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ART 34 AMDT

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Claims

1. A stabilized polymer composition comprising a polymer and an antioxidant composition for improving the long term 5 heat stability of polymers, in particular polyolefins, said antioxidant composition comprising:

(a) 0,01% - 0,5% by weight of at least one sterically hindered phenolic compound, wherein said phenolic compound contains at least one phenolic moiety of general formula (I):

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$$[\text{HO}- (\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{Phenyl})-] \quad (\text{I})$$

wherein R₁, R₂, R₃ or R₄ may be the same or different and at 15 least one of R₁, R₂, R₃ or R₄ is selected from the group consisting of branched alkyl having 1 to 12 carbon atoms, preferably tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl, the others of R₁, R₂, R₃ or R₄ being H or lower alkyl having 1 to 6 carbon atoms;

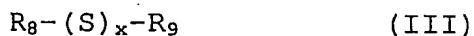
20 (b) 0,01% - 0,5% by weight of at least one phosphorous compound, wherein said phosphorous compound contains at least one phosphorous compound moiety of general formula (II):

$$\text{PX}_1\text{X}_2\text{X}_3 \quad (\text{II})$$

25

wherein X₁ may be R₅ or OR₅, X₂ may be R₆ or OR₆, X₃ may be R₇ or OR₇ and R₅, R₆ or R₇ may be the same or different and at least one of R₅, R₆ or R₇ is selected from the group 30 consisting of C₁-C₂₅ alkyl group, aryl group or aralkyl group which may be substituted by lower alkyl having 1 to 6 carbon atoms, or two or any of R₅, R₆ or R₇ may form a ring structure having 4 to 12 carbon atoms,

(c) 0,01% - 1% by weight of at least one sulphur-containing compound of general formula (III):



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wherein $x = 1$ or 2 , and wherein R_8 and R_9 may be the same or different and are selected from the group consisting of C_{10} - C_{25} alkyl groups optionally being substituted with C_1 - C_{12} alkyl ester carboxylates,

10 wherein said % by weight values are referred to the polymer composition.

2. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition, 15 wherein said antioxidant composition comprises:

(a) 0,02% - 0,2% by weight of said at least one sterically hindered phenolic compound,

(b) 0,03% - 0,2% by weight of said at least one phosphorous compound, and

20 (c) 0,05% - 0,6% by weight of said at least one sulphur-containing compound of general formula (III), wherein said % by weight values are referred to the polymer composition.

25 3. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

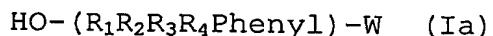
(a) 0,03% - 0,15% by weight of said at least one sterically hindered phenolic compound,

30 (b) 0,05% - 0,15% by weight of said at least one phosphorous compound, and

(c) 0,1% - 0,5% by weight of said at least one sulphur-containing compound of general formula (III),

wherein said % by weight values are referred to the polymer composition.

4. The stabilized polymer composition of any of claims 1
5 to 3, wherein the phenolic compound contains at least one
phenolic moiety of general formula (Ia):



10 wherein R_1 and R_4 being in the 2- and 6-position of the phenol residue may be the same or different and are selected from the group consisting of preferably branched C_1 to C_{12} alkyl, particularly tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl residues, R_2 and R_3 having the meaning as given
15 before, and W is selected from C_1 to C_{12} alkyl, C_1 to C_{12} alkoxy, C_1 to C_{12} alkyl carboxylate or C_1 to C_{12} alkyl substituted by another group of the formula $\text{HO-}(\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{Phenyl})-$, wherein R_1 to R_4 have the meaning as indicated before.

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5. The stabilized polymer composition of any of claims 1 to 4, wherein the phosphorous compound comprises a phosphite moiety of the formula $\text{Bis}(\text{R}_{10})\text{-pentaerythrityldiphosphite}$, wherein R_{10} is selected from $\text{C}_1\text{-C}_{25}$ alkyl group or aryl group
25 which may be substituted by lower alkyl having 1 to 6 carbon atoms.

30 6. The stabilized polymer composition of any of claims 1 to 5, wherein the sulphur-containing compound of general formula (III):



is selected from Di(C₁-C₂₀)alkyl-(S)_x-di-carboxylate wherein the carboxylic acid is selected from C₁ to C₁₂ alkyl carboxylic acids.

5 7. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:

- 2,6-Di-tert.-butyl-4-methyl phenol;
- Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-

10 hydroxyphenyl)-propionate;

- Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;

- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;

15 - 2,2'-Thiodiethylene-bis-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate;

- Calcium-(3,5-di-tert.-butyl-4-hydroxy benzyl monoethyl-phosphonate);

- 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-

20 isocyanurate;

- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl) butanoic acid)-glycolester;

- 4,4'-Thiobis (2-tert.-butyl-5-methylphenol);

- 2,2'-Methylene-bis(6-(1-methyl-cyclohexyl)para-cresol);

25 - N,N'-hexamethylene bis(3,5-di-tert. Butyl-4-hydroxyhydrocinnamamide;

- 2,5,7,8-Tetramethyl-2(4',8',12'-trimethyltridecyl) chroman-6-ol;

- 2,2'-Ethylidenebis(4,6-di-tert.-butylphenol);

30 - 1,1,3-Tris(2-methyl-4-hydroxy-5-tert.-butylphenyl)butane;

- 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;

- 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane;
- 1,6-Hexanediyl-bis(3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene-propanoate);
 - 2,6-Di-tert.-butyl-4-nonylphenol;
 - 3,5-Di-tert.-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris (2-hydroxyethyl)-s-triazine-2,4,6(1H,3H,5H)-trione;
 - 4,4'-Butylidenebis(6-tert. Butyl-3-methylphenol);
 - 2,2'-Methylene bis (4-methyl-6-tert.-butylphenol);
 - 2,2-Bis(4-(2-(3,5-di-t-butyl-4-hydroxyhydrocinnamoyloxy)ethoxyphenyl)propane;
 - Triethyleneglycol-bis-(3-tert.-butyl-4-hydroxy-5-methylphenyl) propionate;
 - Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, C₁₃-C₁₅-branched and linear alkyl esters;
 - 6,6'-Di-tert.-butyl-2,2'-thiodi-p-cresol;
 - Diethyl((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl) phosphonate;
- 4,6-Bis(octylthiomethyl)o-cresol;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)4-hydroxy-, C₇-C₉-branched and linear alkyl esters;
- 1,1,3-Tris[2-methyl-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-5-t-butylphenyl] butane; and
 - Butylated reaction product of p-cresol and dicyclopentadiene.

8. The stabilized polymer composition of any of the
precedent claims, wherein the phosphorous compound is
selected from the group consisting of:

- Tris (2,4-di-t-butylphenyl) phosphite;

- Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite
 - Bis (2,4-di-t-butylphenyl)-pentaerythrityl-di-phosphite;
- 5 - Di-stearyl-pentaerythrityl-di-phosphite;
- Tris-nonylphenyl phosphite;
- Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
- 2,2'-Methylenebis (4,6-di-t-butylphenyl) octyl-phosphite;
- 10 - 1,1,3-Tris (2-methyl-4-ditridecyl phosphite-5-t-butylphenyl) butane;
- 4,4'-Butylidenebis (3-methyl-6-t-butylphenyl-di-tridecyl) phosphite;
- 15 - Bis(2,4-dicumylphenyl)pentaerythritol diphosphite;
- Bis(2-methyl-4,6-bis(1,1-dimethylethyl)phenyl)phosphorous acid ethylester;
- 2,2',2''-Nitrilo triethyl-tris(3,3',5,5'-tetra-t-butyl-1,1'-biphenyl-2,2'-diyl)phosphite);
- 20 - - Phosphorous acid, cyclic butylethyl propandiol, 2,4,6-tri-t-butylphenyl ester; Bis (2,4,6-tri-t-butylphenyl)-pentaerythrityl-di-phosphite;
- 2,2'-Ethylidenebis (4,6-di-t-butylphenyl) fluorophosphonite
- 25 - 6- (3-tert-Butyl-4-hydroxy-5-methylphenyl) propoxy)-2,4,8,10-tetra-tert. butyldibenz (d,t) (1.3.2) dioxaphosphepin; and
Tetrakis-(2,4-di-t-butyl-5-methyl-phenyl)-4,4'-biphenylen-di-phosphonite.
- 30 9. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is selected from the group consisting of:

- Di-stearyl-thio-di-propionate;
- Di-palmityl/stearyl-thio-di-propionate;
- Di-lauryl-thio-di-propionate;
- Di-tridecyl-thio-di-propionate;
- 5 - Di-myristyl-thio-di-propionate;
- Pentaerythritol octyl thiodipropionate;
- Lauryl-stearyl-thio-di-propionate;
- Di-octadecyl-disulphide;
- Di-tert-dodecyl-disulphide and
- 10 - Pentaerythritol-tetrakis-(3-laurylthiopropionate)

10. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:

- 15 - Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;
- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
- 20 - 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-isocyanurate;
- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl)butanoic acid)-glycoester; and
- 25 - 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane.

11. The stabilized polymer composition of any of the preceding claims, wherein the phosphite compound is selected from the group consisting of:

- Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylene-di-phosphonite;

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- Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
 - Di-stearyl-pentaerythrityl-di-phosphite; and
 - Bis(2,4-dicumylphenyl)pentaerythritol diphosphite.

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12. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is Di-stearyl-thio-di-propionate or Di-tert-dodecyl-disulphide.

10 13. The stabilized polymer composition of any of any of the preceding claims, wherein

- (a) the sterically hindered phenolic compound is 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione or pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- (b) the phosphite compound is bis(2,4-dicumylphenyl)pentaerythritol diphosphite; and
- (c) the sulphur-containing compound is Di-stearyl-thio-di-propionate.

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14. The stabilized polymer composition of any of claims 1-13, wherein said composition further comprises metal deactivators and/or UV-stabilisers.

25 15. The stabilized polymer composition of claim 14, wherein said UV-stabilizers are sterically hindered amines.

30 16. The stabilized polymer composition of any of claims 1-16 wherein said polymer is selected from the group consisting of polyolefins, polyethers, polyimides, polyamides and polyesters or mixtures thereof.

17. The stabilized polymer composition of claim 16, wherein said at least one polymer is a homo- or co-polymer of polyethylene, polypropylene and polybutadiene.

5 18. Use of the antioxidant composition as defined in any of claims 1-14 for reducing degradation of a polymeric material during processing and end use of said polymeric material.

10 19. The use of claim 18 for increasing long term thermal stability of the polymeric material.

15 20. Method for producing a polymeric article having an improved long term thermal stability against ageing by radical degradation processes comprising the steps of:

- (a) providing an unstabilised base polymer material;
- (b) adding to said base polymer material the antioxidant composition as defined in any of the preceding claims;
- (c) converting the composition obtained in step (b) in a melt-forming process; and
- (d) confectioning the polymeric material obtained in step (c).

25 21. The method of claim 19 further comprising adding other stabilisers and/or modifiers before the converting step c).

30 22. The method of any of claims 20 or 21, wherein the converting step includes injection moulding, blow moulding, rotational moulding and extrusion.

23. The method of any of claims 20 to 22, wherein the confectioning step includes cutting, lamination and/or welding.

24. Polymeric article having an increased long term ageing stability obtained by the method of any of claims 20-23.